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January 26, 1981

Professor B. L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843

Subject: Effects of deuteration on the  $^{13}\text{C}$  solid state NMR spectra of  
carbohydrates

Dear Professor Shapiro:

Our recent studies concerning the perturbation effects of exchangeable deuterium on the  $^{13}\text{C}$  solution spectra of carbohydrates<sup>1,2</sup> have stimulated us to examine this phenomenon in the solid state. Typically, crystalline carbohydrates exhibit excellent C.P.-M.A.S. narrow line spectra (4-10 Hz at 15 MHz) in the solid state. These spectra have been effectively used to define tautomeric equilibria<sup>3</sup> and conformational states.<sup>4a,4b</sup>

We have examined the 15 MHz  $^{13}\text{C}$  solid state C.P.-M.A.S. spectra of both proteo and deuterio exchanged and recrystallized carbohydrates to evaluate the perturbing effects induced by exchangeable deuterium substitution. As can be seen in Figure A,  $\alpha$ -methyl glucoside crystals in the normal OH state give a well resolved spectrum (8 Hz line width). Upon deuterium exchange and subsequent recrystallization from deuterium oxide, this compound exhibits spectra which have considerably broader lines (20 Hz) and diminished resolution (Figure B). More importantly, however, we observed that the intensity of the resonance corresponding to the C-6 carbon has essentially disappeared. Furthermore, the intensity of this resonance does not respond to changes in the range of contact times (0.5 ms-5 ms) or repetition rates (3-20 sec) studied. This phenomenon has also been observed for  $\beta$ -methyl glucoside.

These findings suggest that exchangeable deuterium induces stronger quadrupolar interactions in primary vs. secondary carbinol carbons. In addition, if intramolecular exchange of labile OD at the primary carbons in the solid state is slow on the NMR time scale, a broad signal could result from a range of shift positions representing varying degrees of deuterium association. This is counter to what one might predict, based on the fact that in solution the most rapid OD exchange takes place at C-6.

Sincerely,

*Philip E. Pfeffer*  
Philip E. Pfeffer

*Kevin B. Hicks*  
Kevin B. Hicks

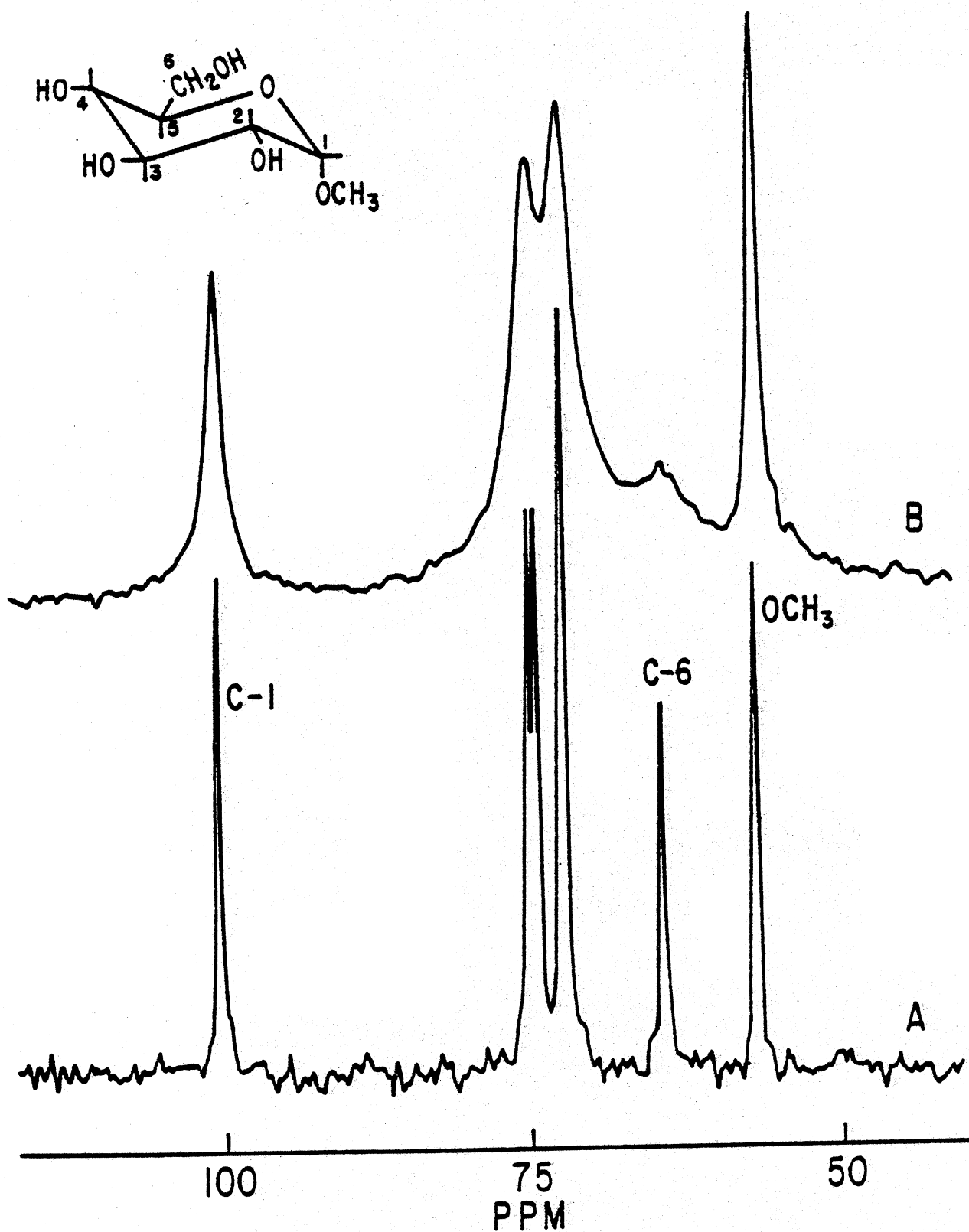
*Kathleen M. Valentine*  
Kathleen M. Valentine

<sup>1</sup> P. E. Pfeffer, K. M. Valentine, and F. W. Parrish, J. Am. Chem. Soc. 101 (1979) 1265.

<sup>2</sup> P. E. Pfeffer, F. W. Parrish, and J. Unruh, Carbohydr. Res. 84 (1980) 13.

P. E. Pfeffer, K. B. Hicks. Abstract. 179th National Meeting of the American Chemical Society, March 23-28, 1980, Carbohydrates paper #26.

<sup>4a</sup> R. H. Atalla, J. C. Cast, D. W. Sindorf, U. J. Bartuska, and G. E. Maciel, J. Am. Chem. Soc. 102 (1980) 3249; <sup>4b</sup> W. L. Earl and D. L. VanderHart, J. Am. Chem. Soc. 102 (1980) 3251.



15 MHz,  $^{13}\text{C}$  C.P.-M.A.S. spectrum of  $\alpha$ -methyl glucoside. Conditions: spectral width = 2000 Hz, contact time = 4 ms, repetition rate = 3 sec, 1000 transients, spinning rate = 2400 Hz.

B. 15 MHz,  $^{13}\text{C}$  C.P.-M.A.S. spectrum of deuterium exchanged and  $\text{D}_2\text{O}$  recrystallized  $\alpha$ -methyl glucoside. Conditions: spectral width = 2000 Hz, contact time = 4 ms, repetition rate = 10 sec, 2500 transients, spinning rate = 2400 Hz.